1. **Project Name:** **Crosscutting Applications for a New Class of Ultra-Hard Materials Based on $AlMgB_{14}$**

2. **Lead Organization:** Ames Laboratory - Metal and Ceramic Science Program
Iowa State University, Ames, IA 50011-3020

3. **Principal Investigator:** Dr. Bruce A. Cook
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4. **Project Partners:** see table (below)

Organization	Type of support	Point of contact
University of Arkansas – Department of Mechanical Engineering.	Subcontract	Prof. Deepak Bhat
Praxair Surface Technologies	In-kind (facilities, testing)	Dr. Thomas Taylor
Kennametal Advanced Solns. Group	In-kind (facilities, testing)	Dr. Dev Bannerjee
Brunner & Lay Inc.	In-kind (facilities, testing)	Dr. Alan Buchanan
Michigan Technological Univ.	In-kind (consultation)	Dr. Marvin McKimpson
Boise Cascade Corp	(in-kind – technical consultation	Dr. Perry Payne
Deere & Co. Technical Center	(in-kind – facilities, testing)	Dr. Bruce Boardman

5. **Date Project Initiated and FY of Effort:** Began: 10/1/01; current fiscal year of project: 2

6. **Expected Completion Date:** 9/30/05

7. **Project Technical Milestones and Schedule:** see table (below)

Task / Milestone Description	Planned Completion	Actual Completion	Comments
Basic processing research - I	ongoing		TiB_2 reinforcement phase (method of addition, distribution)
Powder consolidation studies	ongoing		Fundamental studies to determine optimum consolidation route for highest hardness + wear resistance + toughness (hot pressing vs. press & sinter vs. HIP)
Process scale-up (MA) (I)	12/31/02	12/31/02	Planetary mill (20 – 40 gm quantities)
Mechanical alloying scale-up (II)	3/1/03	6/1/03	Large-capacity Zoz mill (Kg-quantities - delayed due to renovation of laboratory space)
Alloy development – oxidation resistance	12/31/02	ongoing	(phase I) (compositional modification)

Task / Milestone Description	Planned Completion	Actual Completion	Comments
Isothermal oxidation tests	ongoing		Baseline composition completed (testing of modified compositions set to begin 4th quarter FY'03)
Chemical reactivity studies	ongoing		Determination of stability of ultra-hard boride and derivative compounds with various metal-based binder phase materials
Binder phase development	ongoing		An appropriate metal-based binder is needed to enable large-scale Thermal spray applications. In addition, a binder gives the material added toughness, necessary for mining and metal casting applications.
Lathe cutting tests – • 304 stainless steel • 6061 Al • concrete • Ti, Ti-6Al-4V	 12/31/02 12/31/02 12/31/02 ongoing	 12/31/02 12/31/02 12/31/02 ongoing	12/31/02 (phase I) (emphasis shifted to titanium machining applications in response to industrial need)
Microanalytical characterization	ongoing		12/15/02 (phase I)
PLD coating studies	05/01/03	05/01/03	Phase I – feasibility (increased emphasis on this component in response to need for improved MEMS coatings)
HVOF thermal spray trials	ongoing		Delayed – mat'l requirements (processing capability for the requisite Kg-quantities of feed powder came on-line 3/03
Tool design	ongoing		University of Arkansas

8. Past Project Milestones and Accomplishments:

The number and diversity of potential applications for an ultra-hard, wear-resistant, and fracture tolerant material is quite large and continues to expand. Given the limited available resources, it is not currently possible to fully address each application; consequently, we have narrowed our focus during the initial phase of this project, to no more than three key IOF sectors, with the objective of decreasing the laboratory-to-market development time in these critical areas. Specifically, the short-term focus areas include **metal casting** (steel and titanium/titanium alloy production) and **mining** (wear-resistant drilling nozzle, bit, and well liner material). Determination of the properties of $AlMgB_{14}$-based hard-facing coatings (of particular interest to the **agriculture** IOF) is facilitated through the use of pulsed-laser deposition (PLD), which is more amenable to small quantities of powder than traditional large-scale methods such as HVOF. $AlMgB_{14}$ coatings have shown an impressive combination of high hardness, scratch resistance, and low friction coefficient. By understanding the nature of the deposited films and how these films respond to post-deposition heat treatment, we will be in a better position to advance the large-scale thermal spray effort as kilogram quantities of powder become available. In terms of process scale-up, the operational parameters of the recently acquired high-capacity "Zoz" mill have been determined and several 150- to 300 gram quantities of boride were prepared, validating the process. This breakthrough in powder production will enable us to begin HVOF trials in the near future.

This IMF project began in October, 2001, and is addressing seven major focus areas:

1. scale-up studies to increase production quantities from ~4 grams per batch to ~250 - 500 grams per batch
2. optimization of production methods to reduce the variability in hardness and to control deleterious oxygen contamination seen in some early specimens
3. laboratory cutting and grinding tests to quantify $AlMgB_{14}$-based ("BAM") cutting tool performance in controlled comparisons to other commercially available cutting tools (e.g. CBN, diamond, and WC-Co cermets) on a variety of work piece materials
4. development of a metal binder phase to allow production of BAM cermet composite cutting tools similar to the widely used carbide cermets
5. field trials of BAM tools, coatings, and abrasive grits to be performed by cooperating industry partners
6. development and characterization of $AlMgB_{14}$ films prepared by pulsed laser deposition, including lathe cutting test comparisons with un-coated cemented carbide tools.
7. Alloy and compositional research to develop a more oxidation-resistant ultra-hard material than the baseline $AlMgB_{14}$. (There currently exists no material possessing a combination of high hardness at elevated temperature plus oxidation resistance. Successful results from this component will provide significant benefits to a wide variety of industries.)

9. **Planned Future Milestones:**

The recent introduction of the high-capacity Zoz mill to our arsenal of materials processing capabilities provides a means for production of sufficient quantities of $AlMgB_{14}$-based powder to satisfy the requirements of both internal and external applications R&D. Specifically, initial research in the area of hard-facing coatings employed pulsed laser deposition because of its suitability for laboratory-scale specimens. Results obtained from these precursor studies has demonstrated that amorphous boride films can be deposited with the correct stoichiometry, and that crystallization of the hard 1:1:14 phase can be induced by an appropriate heat treatment. The crystallized films were found to possess high hardness (30 to 50 GPa), combined with a low coefficient of friction (~0.05). With the availability of kilogram quantities of powder, spray drying and HVOF coating trials can be performed on various compositions with a high degree of confidence in the chemistry and properties of the films. In addition to thermal spray trials, the increase in powder availability will enable consolidation studies to progress at a significantly faster rate. Preliminary studies suggest that containerless-HIP provides a convenient route to full-densification, and that a significant increase in microhardness can be achieved by eliminating residual porosity. In addition to research on large-scale coatings technology and powder consolidation, the following subtopics will also be addressed during the next fiscal year:

<u>Binder phase development</u> – During FY'04, we plan to optimize the method for addition of the binder and to determine the relationship between binder volume fraction, cermet hardness, toughness, and abrasive wear resistance. In addition, we will characterize the stability of the hard borides in various binder phase compositions, including Co-Mn, by evaluating the diffusion profiles resulting from heat treatments in the 1000°C to 1100°C temperature range. We will also make samples available to our industrial partners for field trials in order to compare performance against their current state-of-the-art materials.

<u>Oxidation-resistant compositions</u> - In FY'03, we initiated the process of applying alloy theory to $AlMgB_{14}$ with the goal of obtaining a material possessing comparable hardness but with improved

oxidation (and corrosion) resistance than that of the parent alloy. Several candidate compounds were hypothesized, and their synthesis and characterization was begun during the third quarter of FY'03. Research in this area will continue in FY'04, with extensive testing of the hardness, wear resistance, toughness, and oxidation resistance of these materials.
Distribution of reinforcement phase – An approach to achieve a finer and more uniform distribution of TiB_2 is currently under evaluation and will be implemented into production materials during FY'04. Consistent with current theories relating hardness to nanostructure, we expect to achieve even higher hardness values from further refinement of phase spacing.

10. **Issues/Barriers:**

Perhaps the most significant technical barrier to progress has been the lack of large (i.e., kilogram) quantities of $AlMgB_{14}$ powder, from which to conduct studies of densification and thermal spray application. With the recent acquisition of a large-capacity Zoz mill, our processing capabilities have been extended from gram-quantities of powder, to multiple-hundred grams quantities during one milling. The appropriate operating variables of this device (speed, cycle periodicity, media-to-charge ratio) have been identified in previous test processing with "BAM" powder, and large-scale production is currently in progress. Implementation of the Zoz device was delayed for several months while laboratory space was renovated to accommodate the device and related equipment.

The lack of a convenient abrasive wear tester has delayed acquisition of wear resistance data on various compositions. We are currently constrained to share a unit supported by the mechanical engineering department; acquisition of our own wear tester would significantly increase optimization of composition and binder phase.

11. **Intended Market and Commercialization Plans/Progress:**

The Iowa State University Research Foundation (ISURF) has teamed-up with ISU researchers to implement a commercialization roadmap for this material, which consists of defining the nature and scope of the license, identifying potential licensees, and initiating contact between the scientific investigators and the licensees. Following a presentation by ISU researchers in April, 2003 to a joint meeting of Viable Technologies, LLC and members of the Iowa Department of Economic Development, in which highlights and preliminary results of the OIT-IMF-sponsored research were outlined, an option agreement for an exclusive license to manufacture ultra-hard $AlMgB_{14}$-based materials was executed with Viable. Viable Technologies, LLC, a company dedicated to local job creation and economic development, has been actively working with our industrial partners to disseminate sample material for evaluation. The company has prepared a business plan summary, which is on record with ISURF. Preparation of the formal business plan is currently in progress and the final version of this document is expected to be available in the August-September, 2003 timeframe.

12. **Patents, publications, presentations:** 7 patent/ROIs + 10 publications + 4 presentations

Patents/ROI's: Provisional Utility Patent Serial No. 60/422,001, "Ductile Binder Phase for Use with $AlMgB_{14}$ and Other Hard Ceramic Materials "; B.A. Cook, A.M. Russell, and J.L. Harringa (ISURF #2949, filed October 29, 2002).

U.S. Patent 6,432,855, "Superabrasive Boride and a Method of Preparing the Same by Mechanical Alloying and Hot Pressing "; (divisional patent of 6,099,605) issued August 13, 2002, B.A. Cook, J. L. Harringa, and A.M. Russell.

U. S. Patent no. 6,099,605, "Superabrasive Boride and a Method of Preparing the Same by Mechanical Alloying and Hot Pressing," issued August 8, 2000, B. A. Cook, A. M. Russell, and J. A. Harringa.

Intellectual Property Disclosure and Record, filed March, 2003, "An Ultra-hard, Low Friction Coating Based on $AlMgB_{14}$ for Reduced Wear of MEMS and other Tribological Components and Systems"; B.A. Cook, A.M. Russell, J.L. Harringa, P. Molian, A.P. Constant, and Y. Tian. (ISURF docket number 03035, AL490).

Intellectual Property Disclosure and Record, filed August, 2002, " A New, Oxidation Resistant, Ultra-hard Material, Aluminum Chromium Boride, $AlCrB_{14}$"; B.A. Cook, A.M. Russell, and J.L. Harringa. (ISURF docket number 2951, AL484).

Intellectual Property Disclosure and Record, filed August, 2002, " A New, Oxidation Resistant, Ultra-hard Material, Aluminum Titanium Boride, $AlTiB_{14}$"; B.A. Cook, A.M. Russell, and J.L. Harringa. (ISURF docket number 2950, AL483).

Intellectual Property Disclosure and Record, filed August, 2002, "Ductile Binder Phase for Use with $AlMgB_{14}$ and Other Hard Ceramic Materials "; B.A. Cook, A.M. Russell, and J.L. Harringa. (ISURF docket number 2949 (AT196)).

Publications/Presentations:

B.A. Cook, A.M. Russell, J.L. Harringa, A.J. Slager, and M. Rohe, "A New Fracture-Resistant Binder Phase for Use with $AlMgB_{14}$ and Other Ultra-Hard Ceramics", Journal of Alloys and Compounds, manuscript submitted April, 2003 (under review).

Y. Tian, A. Constant, C.H.C. Lo, J.W. Anderegg, A.M. Russell, J.E. Snyder, and P. Molian, "Microstructure Evolution of Al-Mg-B Thin Films by Thermal Annealing", Journal of Vacuum Science and Technology A, submitted January, 2003 (under review).

B.A. Cook, J. L. Harringa, T. L. Lewis, B. Lee, and A.M. Russell, "Processing Studies and Selected Properties of Ultra-hard $AlMgB_{14}$", Journal of Advanced Materials, (accepted, scheduled for publication in July, 2003).

J.M. Hill, D.C. Johnston, B.A. Cook, J.L. Harringa, and A.M. Russell, "Magnetization Study of the Ultra-hard Material $MgAlB_{14}$", Journal of Magnetism and Magnetic Materials, accepted (in press).

T.L. Lewis, A.M. Russell, B.A. Cook, and J.L. Harringa, "Al_2MgO_4, Fe_3O_4, and FeB Impurities in $AlMgB_{14}$", Materials Science & Engineering A, Vol. 351, Issues 1-2, pp. 117-122, 2003.

B.A. Cook, J.L. Harringa, A.M. Russell, and S.A. Batzer, "A Proof-of-Concept Study of the Use of Complex Borides for Disassembly of Decommissioned

Nuclear Reactor Containment Vessels", Machining Science and Technology, Vol. 7, No. 1, pp. 139-147, 2003.

A. Russell and B. Cook, "Crosscutting Industrial Applications of a New Class of Ultra-Hard Borides", IMF Newsletter: Industrial Materials for the Future, Winter, 2002, pp. 4-5.

R. Cherukuri, P. Molian, A. M. Russell, and Y. Tian, "A Feasibility Study of Pulsed Laser Deposited, New Superhard Tool Coatings for Metal Cutting," Surface Coatings and Technology, Vol. 155, pp. 112-120, 2002.

A.M. Russell, B.A. Cook, J. L. Harringa, and T. L. Lewis, "Coefficient of Thermal Expansion Determinations for $AlMgB_{14}$", Scripta Materialia, Vol. 46, pp. 629-633, 2002.

Y. Tian, M. Womack, P. Molian, C.C.H. Lo, J.W. Anderegg, and A.M. Russell, "Microstructure and Nanomechanical Properties of Al-Mg-B-Ti Films Synthesized by Pulsed Laser Deposition", Thin Solid Films, Vol. 418, pp. 129-135, 2002.

Highlight

The Problem: A new composite material, $AlMgB_{14} + TiB_2$, has been produced with a hardness of 45 GPa. This extraordinarily high hardness could make this material a less costly and more useful substitute for other ultra-hard materials used in cutting tools and wear-resistant coatings. However, the initial test specimens were small, 3-gram buttons. A scale-up production method is required to produce industrially useful quantities at reasonable cost. In addition, the effects of impurity content, porosity, and phase size on the wear resistance of the material must be determined to optimize performance in bulk material and coatings.

Results Achieved: The project has determined that:

- An industrial-scale Zoz mill horizontal axis milling system can achieve the same level of comminution as a laboratory-scale Spex mill at comparable milling times. This offers a cost-effective method to produce kilogram quantities of the composite.
- The best hardness and wear resistance is displayed in material with the finest phase size (~100 nm), in accordance with the Veprek-Nesdalek hypothesis.
- Porosity sharply lowers wear resistance and fracture toughness.
- Oxygen impurity lowers hardness by forming Al2MgO4 (spinel).
- A transition-metal binder phase has been developed with high strength, high toughness, and good wettability for the AlMgB14 + TiB2 composite (and possibly other hard ceramic materials).
- Pulsed laser deposition has been used to form ultra-hard, adherent, low-friction coatings on Si and Ni, indicating possible use as a coating for MEMS and LIGA systems.

Significance to the Industries of the Future: Many industries perform energy-intensive operations that would benefit from a low-cost, ultra-hard material:

> wood pulping; row-crop and timber harvesting; cutting and grinding of metals, wood, and glass; disassembling decommissioned nuclear reactors; hard-rock mining; trimming sprues and risers in foundries; and constructing roads and buildings

Materials based on $AlMgB_{14}$ have the potential to reduce energy use and other costs in many cutting and grinding operations. Recent analyses have estimated that a 10% market penetration in the metalcasting, mining, and agriculture sectors would result in an energy savings of 5.5 trillion BTUs per year, while reducing CO_2 emissions by at least 2 million metric tons.

Ultra-hard materials such as diamond and cubic boron nitride are expensive and often inappropriate for use in such operations because of chemical reactivity problems, but successful development of this new family of ultra-hard borides will lengthen component lifetimes, lower energy costs, and increase profitability.